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ENTHALPY OF FREE RADICAL POLYMERIZATION OF MALEIC ANHYDRIDE

RAFFAELE GALLO

Istituto di Chimica Industriale, Università di Messina, 98100 Messina (Italy)

FEBO SEVERINI *

Dipartimento di Ingegneria Chimica e Chimica Industriale "G. Natta" del Politecnico,
Piazza Leonardo da Vinci, 32, 20133 Milano (Italy)

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ABSTRACT

The polymerization of maleic anhydride in the presence of benzoyl peroxide or 2,2′-azobisisobutyronitrile was studied by means of differential scanning calorimetry with dynamic and isothermal tests. The absolute ΔH values increase with the percentage of the initiators. The enthalpies of the polymerization reaction in the presence of a large excess of benzoyl peroxide (-85.3 kJ (mol MA)$^{-1}$) or 2,2′-azobisisobutyronitrile (-95.1 kJ (mol MA)$^{-1}$) were obtained by extrapolation.

INTRODUCTION

It is common knowledge that polymers of maleic anhydride can be obtained by polymerizing the monomer in the presence of a radical initiator [1] such as benzoyl peroxide [2] or 2,2′-azobisisobutyronitrile [3]. The reaction proceeds with high amounts of initiator (approximately 10%) producing oligomers. The information on the enthalpy of this reaction is very poor. The molar heat of polymerization of maleic anhydride in the presence of benzoyl peroxide has been reported (58.5 ± 4.2 kJ mol^{-1}) [4].

The aim of this work was to study by differential scanning calorimetry (DSC) the polymerization reaction of maleic anhydride in the presence of benzoyl peroxide or 2,2′-azobisisobutyronitrile.

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* Author to whom correspondence should be addressed.

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EXPERIMENTAL

Materials

Maleic anhydride (MA) (purity better than 99%), benzoyl peroxide (Bz_2O_2) (purified by precipitation in methanol from a chloroform solution; peroxide > 98%) and 2,2′-azobisisobutyronitrile (AIBN) (purity better than 98%) were obtained from Fluka.

Procedure

DSC curves were obtained on a Perkin–Elmer DSC-2 instrument equipped with a Perkin–Elmer thermal analysis data station 3600. Samples of 2–5 mg of the compounds or mixtures of the compounds were weighed in aluminium pans. Covers were placed on the pans; a small hole had been made in the covers to allow the gas generated by reagent decomposition to escape. The instrument was preset at 318 K and the sample was either heated to 573 K at 20 K min^{-1} (dynamic test) or rapidly heated (320 K min^{-1}) to 388 K (isothermal test). Indium was used as the standard for calibrating the temperature axis and the enthalpy output. All experiments were carried out in a nitrogen atmosphere.

RESULTS

Figure 1 shows the change in reaction heat with the molar ratio $R = [MA]/[Bz_2O_2]$. The reaction was carried out under isothermal conditions at 388 K. Preliminary measurements indicated that the reaction did not occur to a measurable extent at temperatures below 383 K. This behaviour agrees with the results of our previous studies [5,6], according to which the decomposition reaction of Bz_2O_2 is perceptible in DSC measurements over 373 K. The high ΔH value of the decomposition of Bz_2O_2 makes the correction of the measured enthalpic values necessary, especially in the case of mixtures containing high percentages of the peroxide. Figure 1 refers to values of ΔH of reaction obtained by subtracting the decomposition ΔH of Bz_2O_2 at that temperature ($\Delta H = -195.1$ kJ mol^{-1}) from the measured value of ΔH. Figure 2 shows a typical DSC curve at 388 K of an MA–Bz_2O_2 mixture with a molar ratio R of 27.5.

Figure 3 shows the uncorrected ΔH values vs. $R = [MA]/[Bz_2O_2]$. The figure indicates that the uncorrected values do not allow us to obtain a finite value when the curve is extrapolated to $R = 0$.

In the case of AIBN, preliminary isothermal measurements gave results which were scarcely reproducible. Dynamic tests produced a regular progress of change in reaction heat with the ratio [MA]/[AIBN] (Fig. 4).

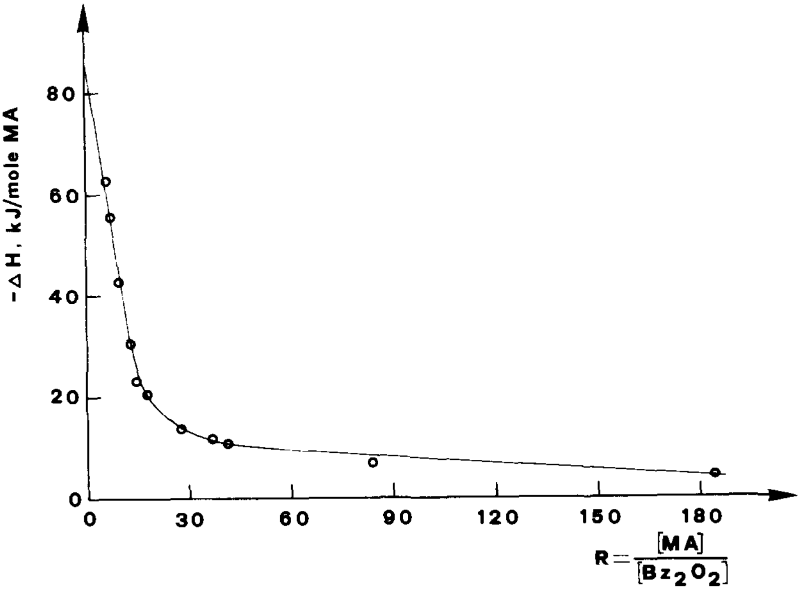

Fig. 1. Change in the reaction enthalpy (corrected for the decomposition enthalpy of Bz_2O_2) with molar ratio $R = [MA]/[Bz_2O_2]$ (reaction temperature, 388 K).

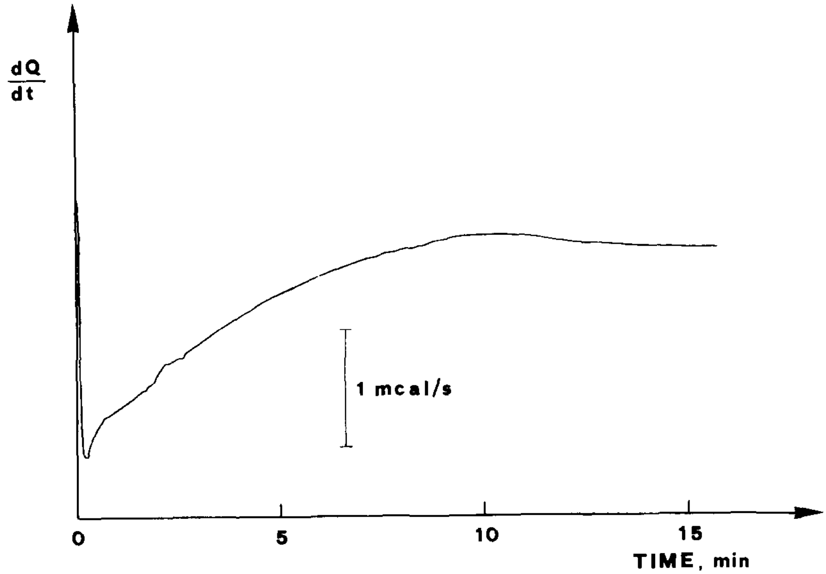

Fig. 2. Typical DSC curve at 388 K of an MA–Bz_2O_2 mixture with $R = [MA]/[Bz_2O_2] = 27.5$.

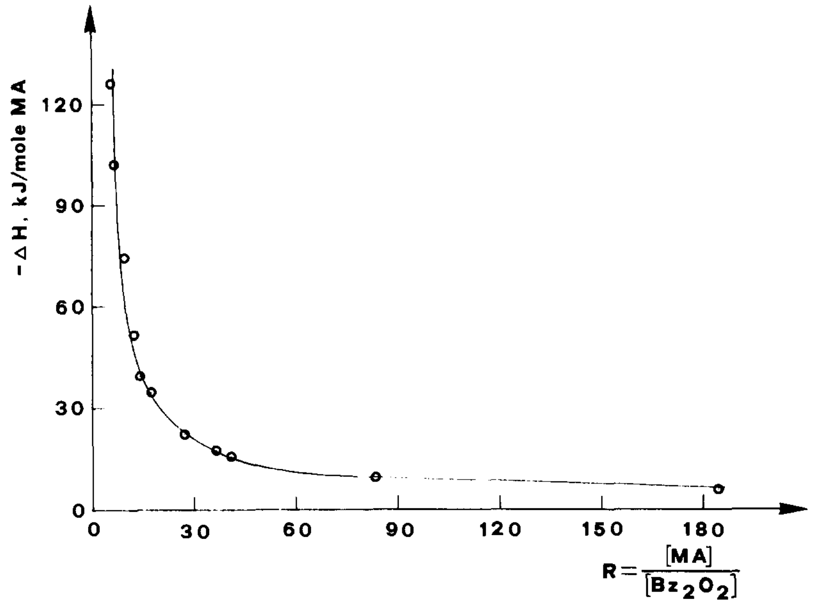

Fig. 3. Change in the uncorrected reaction enthalpy with molar ratio $R = [\mathrm{MA}]/[\mathrm{Bz_2O_2}]$ (reaction temperature, 388 K).

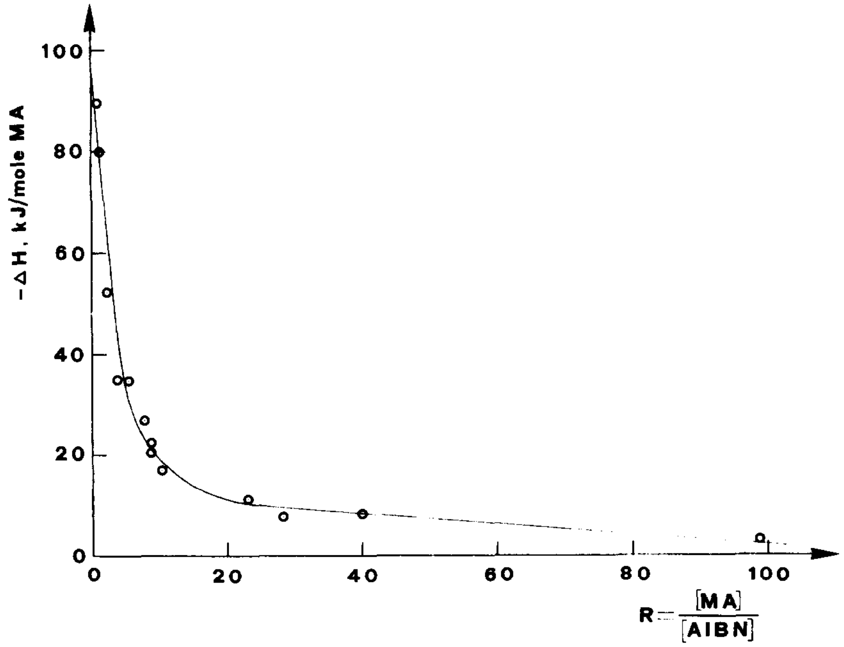

Fig. 4. Change in the reaction enthalpy (corrected for the decomposition enthalpy of AIBN) with molar ratio $R = [\mathrm{MA}]/[\mathrm{AIBN}]$ (scanning rate, 20 K min^{-1}).

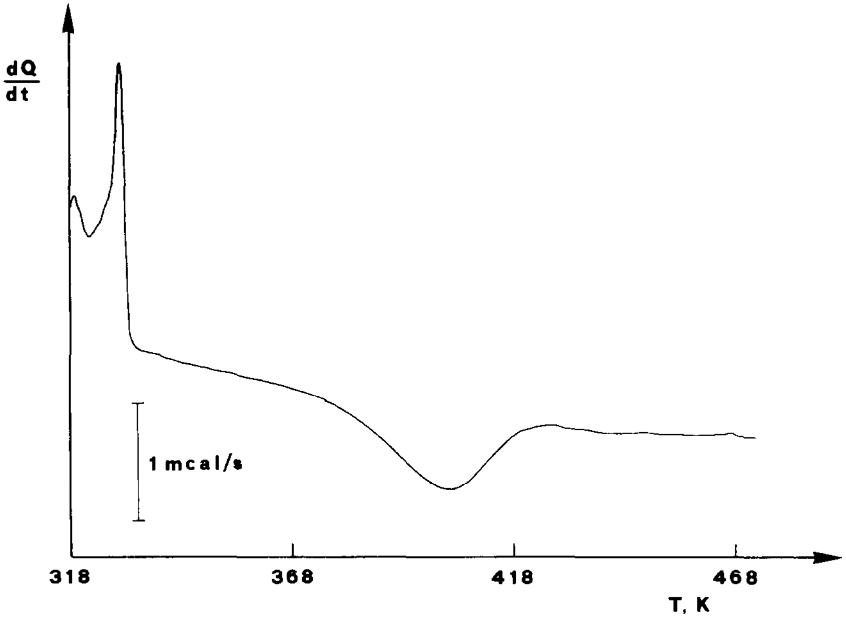

Fig. 5. Typical dynamic DSC curve of an MA–AIBN mixture with $R = [MA]/[AIBN] = 22.9$.

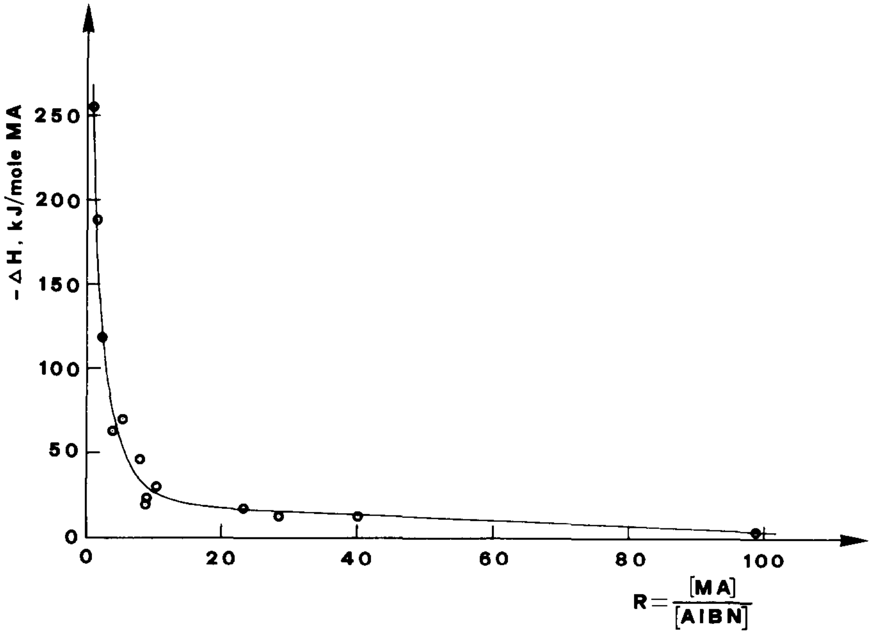

Fig. 6. Change in the uncorrected reaction enthalpy with molar ratio $R = [MA]/[AIBN]$ (scanning rate, 20 K min^{-1}).

The best results were obtained with a scanning rate of 20 K min^{-1}. The decomposition of AIBN is characterized by high ΔH values [5], and so the enthalpic values obtained in the reactions of MA–AIBN mixtures must also be corrected. Figure 4 refers to ΔH values obtained by subtracting the decomposition ΔH of AIBN under the same conditions ($\Delta H = -132.1$ kJ mol^{-1}) from the measured ΔH value. Figure 5 shows a typical dynamic DSC curve of an MA–AIBN mixture with a molar ratio R of 22.9. In this curve, and in the others carried out dynamically, an endothermic peak at 326 K (corresponding to the melting of MA) can be observed before the exothermic peak of the reaction.

Figure 6 shows the uncorrected enthalpic values vs. the ratio [MA]/[AIBN]. As in the case of Bz_2O_2, the uncorrected values do not allow us to extrapolate the curve to $R = 0$.

DISCUSSION AND CONCLUSIONS

Figures 1 and 4 show that the absolute ΔH values increase with a decrease in the molar ratio [MA]/[initiator]. Notable changes are observed from $R = 20$ (approximately 11% by weight) in the case of Bz_2O_2 and from $R = 10$ (approximately 14% by weight) in the case of AIBN. When these curves are extrapolated to $R = 0$ it is possible to obtain the ΔH values of -85.3 kJ $(\text{mol MA})^{-1}$ and -95.1 kJ $(\text{mol MA})^{-1}$ for Bz_2O_2 and AIBN respectively.

The results obtained indicate that the polymerization reaction of MA occurs to a measurable extent only when very high concentrations of the radical initiator are used and that the ΔH value changes with the concentration of the initiator. This behaviour shows that the radical agent, besides acting as an initiator of polymerization, is very active in reactions of chain transfer of the degradative type to the monomer [7]; this explains the formation of polymers of MA with low molecular weight [4].

ΔH values obtained by extrapolating the curves of Figs. 1 and 4 to the zero value of the MA concentration represent the heats generated by the reaction of MA with a very high excess of the radical initiators. At least three terms contribute to these total values: ΔH of the polymerization reaction, ΔH of the chain transfer degradative reactions [7] and ΔH of decarboxylation [8].

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